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Defining the Potential of Nanoscale Re-Os Isotope Systematics Using Atom Probe Microscopy

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Atom probe microscopy (APM) is a relatively new *in situ* tool for measuring isotope fractions from nanoscale volumes (< 0.01 μm^3). We calculate the theoretical detectable difference of an isotope ratio measurement result from APM using counting statistics of a hypothetical dataset to be ± 4δ or 0.4% (2*s*). However, challenges associated with APM measurements (e.g., peak ranging, hydride formation and isobaric interferences), result in larger uncertainties if not properly accounted for. We evaluate these factors for Re-Os isotope ratio measurements by comparing APM and negative thermal ionisation mass spectrometry (N-TIMS) measurement results of pure Os, pure Re, and two synthetic Re-Os-bearing alloys from Schwander *et al.* (2015) (the original metal alloy (HSE) and alloys produced by heating HSE within silicate liquid (SYN)). From this, we propose a current best practice for APM Re-Os isotope ratio measurements. Using this refined approach, mean APM and N-TIMS $^{187}Os/^{189}Os$ measurement results agree within 0.05% and 2*s* (pure Os), 0.6–2% and 2*s* (SYN) and 5–10% (HSE). The good agreement of N-TIMS and APM $^{187}Os/^{189}Os$ measurements confirm that APM can extract robust isotope ratios. Therefore, this approach permits

nanoscale isotope measurements of Os-bearing alloys using the Re-Os geochronometer that could not be measured by conventional measurement principles.

Keywords: Atom probe microscopy, N-TIMS, Re-Os dating, isotopes, method developments, geochronology, *in situ* techniques.

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Highly siderophile elements (HSEs) (Os, Ir, Ru, Rh, Pt, Pd, Re, Au) are important in geochronology and geochemistry. The Re-Os decay system, where ^{187}Re decays to ^{187}Os through emission of β^- radiation with a half-life of 41.6 Ga (Smoliar *et al.* 1996), is particularly useful for determining the timing of geological and cosmological events over the lifetime of the Earth, Solar System (e.g., Allègre and Luck 1980, Day et al. 2016a)), and galaxy (e.g., Luck *et al.* 1980). However, in many cases the carrier phases for these elements are micrometre-to-nanoscale sized metallic alloy particles (see O'Driscoll and González-Jiménez 2016 and references therein). This has led to significant difficulties when measuring bulk samples due to the 'nugget effect' (Day *et al.* 2016b, Meisel and Horan 2016) or for studying multiple alloy populations with different isotopic compositions. On the other hand, *in situ* analyses are challenging due to the scarcity and small size of these alloys. These factors inhibit sensitive isotopic measurements *in situ* because of the limit in the analytical spot size and the number of measurable ions that can be produced and subsequently detected using established techniques (Hutcheon *et al.* 1987, Berg *et al.* 2009, Fischer-Gödde *et al.* 2014).

Laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) can be used to measure isotopic fractions of Re and Os *in situ* with an intermediate precision (Over a given time period) for $^{187}Os/^{188}Os$ within platinum group element reference materials of 0.1% (95% confidence level) when the Re/Os ratio is low ($^{187}Re/^{188}Os < 0.5$) (Nowell *et al.* 2008). However, the smallest spot size that can be achieved with LA-ICP-MS is on the order of 15 µm (González-Jiménez *et al.* 2012). Grains smaller than this are challenging to analyse with LA-ICP-MS due to contributions from neighbouring phases.

Atom probe microscopy (APM) is a high-resolution technique capable of analysing small needle shaped volumes (up to *ca.* 100 nm × 100 nm × 1000 nm) with a sub nanometre spatial resolution (Kelly and Larson 2012). APM can determine the major, minor and trace element (down to 10 appm [atomic parts per million] for sample volumes over 10^6 nm^3) composition of a sample, and characterise nanometre-scale chemical heterogeneities (Kelly and Larson 2012). Data collected by APM record the mass-to-charge-state-ratio (*m/z*) of individual ions following field evaporation from the specimen (Larson *et al.* 2013). The mass resolving power ($m/\Delta m$, where m is the mass-to-charge-state ratio and Δm is the variation in the measured ratio for a single ion) of the atom probe is typically better than 1000 (Larson *et al.* 2013). Therefore, APM is capable of discerning peaks separated by 0.15 *m/z*, commonly referred to as unified atomic mass unit (*u*). This is sufficient to discern isotopic peaks from ions of different charge states (e.g., $^{94}Mo^{3+}$ and $^{63}Cr^{2+}$), but is currently insufficient to determine the mass difference between ions that have the same mass and the same charge (e.g., $^{187}Re^{2+}$ and $^{187}Os^{2+}$). ^{187}Re and ^{187}Os have a difference in mass of 0.000006 *u* (Meija *et al.* 2016a), which requires a mass resolving power > 3×10^7 to distinguish these ionic species. These isobaric interferences are beyond the mass resolving power of any small-scale technique currently available and require either deconvolution calculations to estimate the

contribution of each isotope to the total peak, or element separation based techniques such as the Chicago Instrument of Laser Ionisation (CHILI) (Stephan *et al.* 2016).

The mass resolving power of APM suggests that isotopic analysis of most materials is possible. Several papers have reported isotopic fractions using APM (i.e., Ironside *et al.* 2017, Shimizu *et al.* 2009, Thuvander *et al.* 2011, Shimizu *et al.* 2013, Mukherjee *et al.* 2015, 2016), but only a few have attempted to demonstrate that these fractions are quantitative (i.e., Stadermann *et al.* 2011, Heck *et al.* 2014, Valley *et al.* 2014, Parman *et al.* 2015, Peterman *et al.* 2016). Constraints on the observable size of isotopic variability using APM have not yet been established.

Parman *et al.* (2015) demonstrated that isotopic fractions (with mass fractions < 0.1 g/100 g) of a National Institute of Standards and Technology (NIST) reference material of isoferroplatinum (Pt_3Fe), can be reproduced using APM. Of twenty-five isotopic ratios measured in Parman *et al.* (2015), twenty were within 5% of the NIST values (Parman *et al.* 2015). The high level of accuracy presented in Parman *et al.* (2015), using only minor corrections due to hydride formation, suggests that further evaluation of the methodology will serve to improve the accuracy of isotope ratios measured using APM; for example, in meteoritic nano-diamonds (Berkley *et al.* 1980, Stadermann *et al.* 2011, Heck *et al.* 2014).

During APM analysis, the whole sample is ionised, and it is assumed that there is no bias in the detection of elements or between isotopes of each element, i.e., all species are ionised and detected equally (Kingham 1982, Straub *et al.* 1999). However, unique factors in each APM analysis, such as voltage, tip shape and temperature and their effect on the resulting mass spectrum is not quantified (Parman *et al.* 2015, Reddy *et al.* 2016). In addition, there may

also be small mass dependent isotopic fractionation produced during APM measurements however, thus far these effects have not been observed and are therefore likely to be negligible relative to other sources of uncertainty. It is possible to assess whether the APM measurement protocols are robust by comparing APM measurements with established techniques and reference materials with similar matrix compositions to the unknown material.

This study builds on the work of Parman *et al.* (2015) to quantify the precision and accuracy of isotope ratio measurements possible with APM. Here we analyse alloys of reference material using APM to measure isotope ratios that can be validated with negative ionisation thermal ionisation mass spectrometry (N-TIMS). N-TIMS is a particularly powerful tool for isotope geochemistry as the extended chemical separation procedures prior to isotope ratio measurements removes interfering ions within a given *m/z* range. For Re and Os this is crucial as it allows a direct measurement of the $^{187}Os/^{188}Os$ ratio without the isobaric interference of $^{187}Re^{+}$. The samples included simple, single element alloys through to complex multi-HSE alloys from Schwander *et al.* (2015). These APM analyses are used to devise an approach that reliably reproduces isotopic ratios of known samples. It is our hope that this approach can then be applied to finite Os-rich materials and minerals that are too small for conventional measurement principles such as sub-micrometre refractory metal nuggets in meteorites (Palme and Wlotzka 1976, Wark and Lovering 1976) or adapted to observe nucleosynthetic variations in tiny interstellar particles or pre-solar grains (e.g., Croat *et al.* 2013, Stadermann *et al.* 2011)

Methodology

Samples

The reference materials analysed in this study were a pure Re wire, a pure Os wafer, and synthetic multi-HSE alloys from Schwander *et al.* (2015) including the primary ingot henceforth referred to as 'HSE1 and HSE2', and the experimental product of heating within a silicate liquid henceforth referred to as 'SYN1 and SYN2'. Both alloys are composed of Os, Re, Ir, Ru, Pt, Mo, W, Fe and Ni (Figure 1).

Sample preparation

A small portion of the Re wire, Os wafer, and original multi-HSE alloy of Schwander *et al.* (2015) were separated from the main mass using pliers (Re wire and Os wafer), or a diamond wire saw (multi-HSE alloy), for N-TIMS analysis. APM specimens were prepared from the remaining Re wire (Re1 and Re2), Os wafer (Os1) (Figure 2), and multi-HSE alloy (HSE1 and HSE2) (Figure 3). In addition the final alloy nuggets formed within a silicate liquid during the heating experiments of Schwander *et al.* (2015) were also prepared for APM (SYN1 and SYN2) (Figure 4). APM specimens were extracted following the lift out approach described in Thompson *et al.* (2007), and shaped using the Tescan LYRA 3 Ga^{+} focused-ion beam scanning electron microscope (FIB-SEM) at the Advanced Resource Characterisation Facility (ARCF), John de Laeter Centre, Curtin University. The FIB was operated using an accelerating voltage of 30 kV for the lift out and specimen sharpening and finished with a 2

kV polishing step to remove the outer layer of Ga implantation. Methodology specific to this instrumentation has been described elsewhere (Fougerouse *et al.* 2016, Peterman *et al.* 2016).

Atom probe microscopy (APM)

APM specimens Os1, Re1, Re2, HSE1, HSE2, SYN1 and SYN2 were analysed in laser mode on the Cameca local electrode atom probe (LEAP) 4000X HR Geoscience Atom Probe, at the ARCF, John de Laeter Centre, Curtin University. The operating conditions including Laser energy, pulse rate, specimen temperature, evaporation rate and counts measured are detailed in Table 1. The bulk chemistry of each sample (Table 2) was calculated from the resultant mass-to-charge-state-ratio spectrum by measuring all the counts under the isotope peaks of each element from the point where the peak rises above the background noise to where it descends below the background noise.

Negative ionisation thermal ionisation mass spectrometry (N-TIMS)

The Os isotopic composition was analysed in the John de Laeter Centre at Curtin University (Perth, WA). In order to achieve a complete digestion of the pure Os metal and the multi-HSE alloy, we applied the Carius tube digestion method modified from Shirey and Walker, (1995). Approximately 0.5 mg of Os metal and multi-HSE alloy were consumed. The acid digestion was done using concentrated acids (1 ml of purged double-distilled HNO_3 and 3 ml of triple-distilled HCl). This mixture was chilled and sealed in previously cleaned Pyrex^{TM} borosilicate Carius Tubes (CT) and heated up to 220 °C for 60 h. Osmium was extracted from the acid solution by chloroform solvent extraction (Cohen and Waters 1996), then back-extracted into HBr, followed by purification via microdistillation (Birck *et al.* 1997). The

purified Os fraction of each sample was loaded onto two separate Pt filaments, and measured using N-TIMS on a ThermoFisher Triton^{TM} mass spectrometer using Faraday cup collectors. The beam for samples studied was maintained at 1×10^{-11} A (for ^{192}Os) for extended period of time for Os metal (100 blocks of ten cycles were collected), allowing to obtain a standard error of the mean precision bellow 10 ppm level (Birck 2001). For HSE alloy sample, ten blocks of ten cycles were collected, allowing standard error of the mean precision at 10–20 ppm level. The measured isotopic ratios were corrected for mass fractionation using $^{192}Os/^{188}Os = 3.083$ from the *m/z* 240/236 ratio ($^{192}Os^{16}O_3/^{188}Os^{16}O_3$).

The pure Os metal was analysed two times on two separate filaments, giving the average of 0.14178 ± 0.00007 (95% confidence). The multi-HSE alloy was also analysed twice in static mode at 0.3–0.4 V for ^{188}Os, collecting ten blocks of ten cycles each. The average was 0.10704 ± 0.00005 (95% confidence) (Table 3). The pure Re metal used for the atom probe experiment represents an in-house Re reference material made from zone refined Re filament. Its $^{187}Re/^{185}Re$ ratio is estimated by measurement of ReO_4^- at masses 249 and 251 *u* to be 1.6703 ± 0.0008 (*n* = 12, 95% confidence).

To monitor the intermediate precision over a period of 12 months of the N-TIMS instrument for Os, an AB-2 Os reference solution (University of Alberta) was measured as part of the protocol. The AB-2 Os standard yielded 0.10687 ± 0.00012 (95% confidence) during the 12 month period of the measurements, which is consistent with that reported by Selby and Creaser (2003) (0.10684 ± 0.00004). The total procedural blank for Os was 0.50 pg; its contribution is insignificant for the samples studied. The $^{187}Os/^{188}Os$ ratio for the blank was 0.201 ± 0.020.

The Os ratios were recalculated for ^{189}Os to be consistent with the atom probe analysis using the $^{188}Os/^{189}Os$ ratio detailed in Meija *et al.* (2016b). The results of each measurement are given in Table 4.

Theoretical constraints on the APM technique

During APM analysis it is usually assumed that every atom within a specimen tip is ionised with an equal likelihood, and every ion has an equal chance of detection regardless of elemental species or atomic weight (Kelly and Larson 2012). Other time of flight (ToF) techniques where there is incomplete ionisation must be corrected for isotopic mass fractionation (Guillong and Günther 2002). These effects are not expected to occur in APM (Parman *et al.* 2015).

In an ideal APM acquisition, the only source of uncertainty is derived from the chance of detection for an individual atom, which can be described by standard counting statistics (Larson *et al.* 2013). In the following section we explain how the precision of APM datasets varies with counts and determine the theoretical precision possible with the technique, and the size of isotopic variations that may be detected

Counting statistical uncertainty

Uncertainties in APM measurement results can be calculated using three methods: (1) counting statistics (Larson *et al.* 2013), (2) comparing the APM measurements of a known reference material (i.e., Parman *et al.* 2015), or (3) comparing APM measurements to another

more established approach (i.e., Valley *et al.* 2014). Here we use a combination of all three methods. The calculated uncertainty from the counting statistics in APM measurements is expressed as the standard deviation (*s*) described by Equation (1) (Larson *et al*. 2013):

$$\boldsymbol{s} = \sqrt{\boldsymbol{A} + \boldsymbol{B}} \qquad (1)$$

Where A is the total counts detected from a single ranged peak, including the background, and B is the average background counts. The contribution of background counts (B) within the peak range is estimated by measuring the spectrum counts in a nearby range that is free from mass peaks and dominated by background noise. For all data presented in this section we propagated the 2s calculated uncertainty from equation 1 for the measurements of each ion peak. The precision of the APM measurement improves with the number of counts detected and the relative uncertainty decreases. This relationship can be expressed as a power law (Equation (2)).

$$\boldsymbol{2s_A = 200\frac{1}{\sqrt{A}}} \qquad (2)$$

where A is the total counts detected, and s_A is the relative uncertainty expressed in % of the counts. The uncertainties associated with low counts ($< 10^3$) are large, but improve significantly with higher counts (Figure 5). Counts > 10^6 from a single *m/z* peak have an associated relative uncertainty < 0.2%, and counts > 10^8 from a single *m/z* peak have associated uncertainties < 0.02% (Figure 5). The theoretical sensitivity of APM at high

counts would therefore be comparable to secondary ion mass spectrometry (SIMS), sputtered neutral mass spectrometry (SNMS), N-TIMS, glow discharge mass spectrometry (GDMS) and inductively coupled plasma-mass spectrometry (ICP-MS), which have associated precisions of ± 0.02–1% for single ion collectors (Becker 2002).

Equation 2 does not take into account the background counts in the spectrum as well as other systematic sources of uncertainty in the APM acquisition such as detector dead times, subtle peak overlaps, interferences, etc.; therefore, more realistic measurement uncertainty estimates will be higher. The white-noise background should remain essentially constant in the time-of-flight (ToF) spectrum, which corresponds to a decaying global background in the *m/z* spectrum (Hudson *et al.* 2011, Larson *et al.* 2013). The average background in APM datasets over a 0.2 *u* peak range width from this study was < 100 counts. In this work, the background contribution to the calculated precision is considered negligible where $A > 10B$ (Figure 5). Where $A \leq B$, the relative precision is significantly higher than predicted by Equation (2) (Figure 5) and so Equation (2) is only used where measured counts in the peak are larger than the background counts by one order of magnitude (Figure 5).

Theoretical sensitivity of isotopic fraction measurements

The relationship between counts and their uncertainties calculated from Equation (1) and Equation (2) can be used to estimate the size of an isotopic deviation from a particular reference frame detectable with APM, for an ideal case. In this work we will use delta (δ) notation described by Equation (3) (Schaefer 2016, Yokoyama and Walker 2016):

$$\boldsymbol{\delta} = \left[\frac{\left(\frac{^1X}{^2X}\right)_{sample}}{\left(\frac{^1X}{^2X}\right)_{standard}} - \mathbf{1}\right] \times 1000 \qquad (3)$$

This can be expanded to form a general case (Equation (4)) by combining Equations (1) and (3) whereby the uncertainty of an APM measurement for a given number of ion counts of the respective isotopes ^{1}X and ^{2}X of element X can be expressed in δ notation.

$$\boldsymbol{\delta} = \left[\frac{\left(\frac{(^1X \pm 2s_{1_X})}{(^2X \pm 2s_{2_X})}\right)_{sample}}{\left(\frac{^1X}{^2X}\right)_{standard}} - \mathbf{1}\right] \times 1000 \qquad (4)$$

If ^{1}X and ^{2}X have the same relative fraction whereby ^{1}X/^{2}X = 1 we can apply Equation (4) to visualise the sensitivity of the technique with increasing counts (Figure 6). Low counts (< 10^3) result in large uncertainties (± > 100δ), whereas high count rates (> 10^6) are more precise and could discern isotopic variations of ± > 4δ (Figure 6). Isotopic variations of comparable size are observed in meteoritic components for a number of elements (Yokoyama and Walker 2016), and isotopic variations in pre-solar grains are greater still (Nittler 2003, Zinner 2003). Therefore, the sensitivity of the APM technique has the potential to detect these isotopic variations.

Evaluation of data reduction methods using pure Re and Os metals

The constraints calculated above are for an idealised case for a simple sample. Geological and meteoritic samples are more complex, containing several elements in major, minor and trace mass fractions that populate the *m/z* spectrum with several peaks. The APM technique also produces monoatomic ions with multiple charge states, and polyatomic ions such as hydride ions, molecular ions, and isobaric interferences (Kelly 2011, Thuvander *et al.* 2011, Larson *et al.* 2013, Heck *et al.* 2014), which affect the *m/z* spectrum and must be identified, quantified, and corrected. Furthermore, for quantitative analysis of APM data, there are currently no standardised data reduction methods, such as for peak ranging, assessing and correcting any hydride contribution, or which isotope to use for the deconvolution.

Pure Re (Re1 and Re2) and pure Os (Os1) APM specimens were reduced in order to assess the effect of the peak ranging, hydride formation and multiple charge states on the measured isotopic fractions. For Os, only the stable isotopes and radiogenic ^{186}Os were evaluated. This allows us to determine which data-reduction methods accurately reproduce isotopic measurements as measured by N-TIMS.

The effect of ranging methods

To calculate the abundance of counts under a mass peak a range of *m/z* values is selected. Peaks can be ‘ranged’ in this way using multiple methods. Several methods have already been evaluated by Hudson *et al.* (2011). Here we will describe and discuss the advantages

and limitations of two methods: the full-width method (R6 in Hudson *et al.* (2011)), and the constant-width method (an expansion of R5 in Hudson *et al.* (2011)).

The full width method: For the full width method, peaks are ranged from where they first emerge above the background level to where they descend below the background (Hudson *et al.* 2011) (Figure 7). This method is advantageous as it includes a large proportion of the counts belonging to the mass peak. However, it will also include contributions from neighbouring peaks, background noise, and peak tails, which may result in an overestimate of the species of interest within the measured peak.

The constant width method: The constant width method is an expansion of the max bin method used in Hudson *et al.* (2011). In the method used here, the smallest peak of the element is identified and ranged so the entire range is above background when centred over the peak apex. The remaining isotope peaks are ranged using the same width centred over the apex of the peak (Figures 8 and 9). The peak widths used in each case are: Os1 = 0.25 *u*, Re1 = 0.35 *u* and Re2 = 0.20 *u*. This method neglects counts present on the limbs of each peak, resulting in lower total counts and higher calculated uncertainties than the full width method. However, the relative contributions from neighbouring peaks and background noise are reduced. With the reasonable assumption that peak shapes are the same between isotopes of the same element, this ranging method is expected to yield the same proportion of counts for each mass peak. This approach avoids the bias introduced when higher peaks are ranged with a larger width, and is not affected by variations in the peak shape, such as peak broadening, or long peak tails, outside of the central range. These factors often cause overestimations when using methodologies that treat each peak individually – such as the full

width method, and also any full-width-half-maximum ranging methods (Hudson *et al.* 2011) in which the range width is also dependent on the peak height. Furthermore, our constant width method is more desirable than the max bin method (Hudson *et al.* 2011) as it incorporates more counts, reducing the calculated uncertainties.

Evaluation of ranging methods: APM data from Os1 was reduced using both ranging methods (Figures 8 and 9). The relative fraction of the stable Os isotopes was calculated and compared with expected IUPAC fractions (Meija *et al.* 2016b) (Figure 10). Both methods produced the expected Os isotopic fractions to < 0.5%. This is within the calculated uncertainties (2*s*), and also consistent with N-TIMS measurements (Figure 10). However, the constant width method is more accurate for the majority of Os isotopes (Figure 10).

The effect of ionic species

Atom ionisation occurs during field evaporation in APM. The ionic charge of an atom can be variable, causing emission of atoms in several charge states ($^{+}$), ($^{2+}$), or ($^{3+}$). This is due to the difference in the field-strength required for single and multiple ionisation of each element (Tsong 1978). The Re1 and Re2 datasets contain Re ions in the ($^{2+}$) and ($^{3+}$) charge state; ($^{+}$) ions were not observed. The data were reduced using the constant width method, and the Integrated Visualisation and Analysis Software (IVAS) background correction, for Re^{2+} and Re^{3+}. The $^{187}Re/^{185}Re$ ratios were consistent with the expected IUPAC ratios and N-TIMS measurements, within calculated uncertainties (2*s*) (Figure 11). Although uncertainties associated with the ($^{3+}$) ions are larger due to smaller count totals, isotopic fractionation

between charge states is not observed. Therefore, multiple charge states do not need to be taken into account to measure true isotopic fractions, and regions of the spectrum can be chosen that contain charge states for elements where there are fewer isobaric interferences and significant counts for the isotopes of interest.

Hydride formation

The formation of hydride ions is sometimes observed in APM acquisitions (Miller and Forbes 2014), and recent geological APM analyses have reported the formation of charged hydride molecular ions (e.g., Heck *et al.* 2014, Parman *et al.* 2015). These are thought to arise from H_2 present in the ultra-high vacuum environment adsorbing on the tip surface, with some elements forming hydride polyatomic ions more readily than others (Kelly 2011). When present, hydrides of lighter ions can contribute to the peaks of heavier ions causing an apparent biasing of the data. Parman *et al.* (2015) reported contributions from hydrides of Pt of ~ 0.4% for each peak. These contributions are significant and will increase the ion counts of isotope peaks 1 *u* heavier for $^{+}$ ions and 0.5 *u* heavier for $^{2+}$ ions etc.

The *m/z* spectra of Os1, Re1 and Re2 do contain small peaks of Os-H or Re-H 0.5 *u* above the heaviest isotopes (Figure 8 and 9). The peaks associated with hydride polyatomic ions were ranged using the full width method due to their small size, and after an IVAS background correction was calculated, the hydride peaks were found to contain < 100 counts. Every isotope of an element may be considered to have an equal chance of forming a hydride ion, as the polyatomic ions are understood to form through a mass-independent chemical process (Kelly 2011). We can therefore compare the size of the hydride peaks with the size of

the single ion peak and conclude that for Re and Os < 0.02% of each isotope form hydride polyatomic ions, which is less than the calculated uncertainty (2*s*) of the measurement result.

Evaluation of data reduction methods from complex HSE alloys.

Deconvolution of peak overlaps

One challenge with isotopic analysis of *m/z* spectra is the presence of isobaric interferences between isotopes of different elements that have the same *m/z* ratio. This is particularly challenging in geological samples, which contain a variety of major, minor and trace elements; several isobaric interferences may be present in the APM *m/z* spectra (Heck *et al.* 2014, Valley *et al.* 2014, Fougerouse *et al.* 2016, Pérez-Huerta *et al.* 2016, Weber *et al.* 2016, White *et al.* 2017) (Figure 12). These isobaric interferences can be deconvolved using Equation (5) if the relative fraction of one of the isotopes for the overlapping peaks is known or can be assumed.

$$^{i}\boldsymbol{X} = \ ^{i}\boldsymbol{A} - \left[\left(\frac{^{j}Y_{A}}{^{j}Y_{standard}}\right)\ ^{i}\boldsymbol{Y}_{standard}\right] \qquad (5)$$

^{i}A is the total counts in an *m/z* peak containing counts of overlapping isotopes from elements X and Y of mass 'i'. 'j' denotes another isotope of element Y that does not have an associated isobaric interference. $^{j}Y_{standard}$ and $^{i}Y_{standard}$ are the known relative IUPAC normalised fractions of ^{j}Y and ^{i}Y and $^{j}Y_{A}$ is the total counts in the *m/z* peak of isotope '*j*', all of which come from element Y. This calculation can only be performed if the isotopic normalised

fractions are known. Therefore, it is not possible to apply Equation (5) to the calculation of radiogenic daughter products, or to samples that exhibit isotopic fractionation. Furthermore, the isotope used in the correction cannot also be affected by an isobaric interference of its own.

We reduced the HSE1 and HSE2 APM datasets using the IVAS automated background correction and the constant width method. Hydride contributions to the spectrum were comparable to those calculated above and were ignored. These data contain a number of isobaric interferences, which were corrected to evaluate the effect that the choice of isotope, the choice of element, and contributions from 'hidden' overlaps on the accuracy of isobaric interference deconvolution. We focused on the 90–102 *u* region of the *m/z* spectra, which contained Os^{2+}, with the aim of providing a 'best practice' methodology for the deconvolution of isobaric interferences in APM.

The choice of element for deconvolution: In this section, we examine the effect of the element used to deconvolve isobaric interferences. Osmium ions have several known isobaric interferences with other HSEs ions at all charge states: ^{190}Os and ^{192}Os overlap with ^{190}Pt and ^{192}Pt, while ^{184}Os and ^{186}Os overlap with ^{184}W and ^{186}W and ^{187}Os overlaps with ^{187}Re. To evaluate the accuracy of each method we will only assess the stable isotopes of Os, so as ^{187}Os is a radiogenic isotope, we will not incorporate it into our assessment of these deconvolution methods. It should be noted that ^{186}Os is also a radiogenic isotope from the decay of ^{190}Pt. Here we treat it as a stable isotope as ^{186}Os isotopic variations are generally small and as will become apparent in the following section the ^{186}W correction to determine ^{186}Os fractions result in large uncertainties.

The ^{184}Os-^{184}W and ^{186}Os-^{186}W isobaric interferences within the HSE1 data set in the 2+ charge state were resolved firstly assuming IUPAC fractions of ^{183}W or ^{182}W to provide deconvolved fractions for ^{184}Os and ^{186}Os. The ^{184}Os-^{184}W and ^{186}Os-^{186}W isobaric interferences were also resolved assuming IUPAC values of ^{189}Os (Meija *et al.* 2016b), to provide deconvolved fractions for ^{184}W and ^{186}W. These deconvolutions were calculated without accounting for contributions from Pt^{2+}. After assessing the results of these deconvolutions, the ^{190}Os-^{190}Pt and ^{192}Os-^{192}Pt isobaric interferences were resolved assuming IUPAC fractions of ^{195}Pt (Meija *et al.* 2016b) (Figure 13). For each of these deconvolutions, the Os isotope fractions were renormalised to 98.04 (the total IUPAC fractions of the non-radiogenic isotopes of Os) and compared with their expected IUPAC relative fractions (Meija *et al.* 2016b) (Figure 13).

In the 2+ charge state the ^{183}W or ^{182}W corrections produce large anomalies for ^{184}Os and ^{186}Os, including an impossible negative fraction of ^{184}Os, when deconvolved using ^{182}W (Figure 13). The Os correction forces the ^{184}Os and ^{186}Os to be in agreement with their IUPAC ^{189}Os relative fractions. The large anomalies in the W deconvolution are caused by the high fraction of ^{184}W and ^{186}W relative to ^{184}Os and ^{186}Os (Meija *et al.* 2016b). Therefore, the isotope with the lowest expected peak contribution should be chosen to perform the deconvolution. However, if isotopic variations are present in the sample this information will be lost from the element used in the correction. Consequently, the fractions of the other isotope in the isobaric interference will represent the sum of the variations present in both isotopes.

Following this method, the ^{190}Os-^{190}Pt and ^{192}Os-^{192}Pt isobaric interferences in the 2+ charge state were resolved assuming IUPAC fractions of ^{195}Pt (Meija *et al.* 2016b). Since Pt has a low mass fraction in the sample, and ^{190}Pt and ^{192}Pt have low relative fractions compared with ^{195}Pt, the interferences with ^{190}Os and ^{192}Os will be small but easy to estimate. $^{195}Pt^{2+}$ was chosen as opposed to other Pt^{2+} isotopes as it is an odd-numbered isotope, which is advantageous for the reasons outlined below (*Other overlapping ions*). This deconvolution, unlike the Os deconvolution above, has the benefit of producing 'real' (deconvolved) values for $^{190}Os^{2+}$ and $^{192}Os^{2+}$. However, this correction drives Os isotopic relative fractions away from IUPAC values (Figure 13). This could be due to a number of factors; an isobaric interference in the ^{195}Pt peak will overestimate ^{190}Pt and ^{192}Pt and consequentially underestimate ^{190}Os and ^{192}Os. Additionally, Os^{2+} isotopes may have isobaric interferences causing them to appear enriched. However, even with these simple corrections, the Os^{2+} isotopes are within 1% of the relative difference from the expected isotopic fractions and within the calculated uncertainties. Therefore, any other contributions from other sources are likely to be small.

Utilising the isotope with the lowest fraction is not appropriate in all cases, particularly when the uncertainty in the isotopic fraction itself may be large. In the ^{187}Re-^{187}Os overlap, ^{187}Os is the radiogenic daughter product of ^{187}Re (Geiss *et al.* 1958, Herr *et al.* 1954, Hintenberger *et al.* 1954, Naldrett and Libby 1948), so for geological samples ^{187}Os will be variable and contingent on the ^{187}Re mass fraction. As these mass fractions are used in radiometric dating (Geiss *et al.* 1958, Herr *et al.* 1954, Hintenberger *et al.* 1954, Naldrett and Libby 1948), they cannot be assumed to have standard values. However, Re isotopic relative fractions are relatively consistent across a range of geological and meteoritic samples (Luck *et al.* 1980, Anders and Grevesse 1989, Walczyk and Heumann 1993, Lodders 2003, Meija *et al.* 2016b),

with only small variations of < δ0.14 observed (Liu *et al.* 2017). So, although ^{187}Os has a lower mass fraction, ^{187}Re, ^{185}Re and ^{187}Re should be used to deconvolve the isobaric interference to produce a 'real' fraction of ^{187}Os. The relative fraction of $^{187}Os^{2+}$ in HSE1, HSE2, SYN1 and SYN2 is significantly lower (1.3 ± 0.08%) than the present day ^{187}Os isotope fraction (1.96%) (Meija *et al.* 2016b) (Table 4).

The choice of isotope: Some elements have several isotopes that could be used in the deconvolution of isobaric interferences; Os has seven (Aston 1931, Nier 1937). We have deconvolved the ^{184}Os-^{184}W and ^{186}Os-^{186}W isobaric interferences in the 2+ charge state of HSE1 assuming IUPAC relative fractions for ^{188}Os, ^{189}Os, ^{190}Os and ^{192}Os to determine how the choice of isotope affects the calculated isotopic fractions (Figure 14). The $^{189}Os^{2+}$ deconvolution is closest to the expected IUPAC isotopic fractions for ^{184}Os and ^{186}Os. However, the other Os isotopes with relatively larger fractions; i.e., $^{190}Os^{2+}$ and $^{192}Os^{2+}$, produce more counts and therefore are more precise. These isotopes should theoretically be closer to IUPAC values. However, this is not the case, as isobaric interferences associated with these isotopes may not be accounted for.

Other overlapping ions: It is plausible that there may be elements of different charge states or molecular ions, other than Os^{2+}, Re^{2+}, W^{2+} and Pt^{2+}, present in this region of the *m/z* spectrum, which have not been accounted for. The 90–100 *u* range in the *m/z* spectrum may contain contributions from Mo^{+} and Ru^{+} isotopes. If these are present, they will cause overestimations in $^{184}Os^{2+}$, $^{188}Os^{2+}$, $^{190}Os^{2+}$ and $^{192}Os^{2+}$ fractions. In the case of Ru^{+}, several peaks should not overlap; i.e., $^{100,101,102,104}Ru^{+}$, so their contributions can be calculated using the method described above (*Deconvolution of peak overlaps*). However, for

Mo^{+}, all isotopes in this region of the spectrum overlap with other isotopes. Peak overlaps may also be caused by complex ions such as Mo_2^{2+} etc. In fact, there are a large number of combinations and charge states that can produce a wide range of *m/z* values. However, only a limited number of these are realistic. From the pure samples of Os1, Re1 and Re2, a ($^{2+}$) charge state is the dominant emission, with minor contributions from ($^{3+}$) ions in the *m/z* spectra; ($^{+}$) ions are not observed, under what are expected to be similar field-evaporation conditions to the alloy samples (Kingham 1982). This, coupled with the good correlation between the Os and IUPAC isotopic fractions, for these samples, suggests that if these contributions are present they are small. However, there are slight enrichments (< 0.4%) of $^{188}Os^{2+}$ and $^{190}Os^{2+}$ in HSE1 relative to IUPAC fractions, which may hint at the presence of Mo^{+} (Figure 13 and 14). If Mo^{+} ions are present to even a small degree, it is possible to eliminate interference, as $^{189}Os^{2+}$ does not have an isobaric overlap. This is because ^{189}Os in the ($^{2+}$) charge state is at 94.5 *u* in the *m/z* spectra; so no ion in the ($^{+}$) or ($^{3+}$) charge state can overlap. The only possible overlaps for these peaks are generated by a molecular ion with a mass of 189 *u* in the ($^{2+}$) state, or a mass of 378 *u* in the ($^{4+}$) charge state. There are only a few elements combinations possible from those present in the sample, and none of these polyatomic ions are detected in any other region of the *m/z* spectrum. Therefore, the species that should be used to separate overlapping isotope peaks are odd numbered isotopes in the ($^{2+}$) charge state, as they have a reduced chance of being affected by isobaric interferences.

Method validation

APM analysis of multi-element samples from the same material may produce different peaks in the *m/z* spectra over separate analyses. This may be the result of subtle variations in the measurement conditions. Osmium isotopic data was reduced using the methods described

above for HSE1 and HSE2 (Figure 15). These reveal that within the calculated uncertainty (2*s*), the Os measurement results of both samples are the same, and consistent with expected IUPAC values. This implies that APM consistently detects isotopic fractions for materials from the same sample.

Comparison with N-TIMS

The $^{187}Os/^{189}Os$ ratio of the bulk HSE alloy, recalculated from the $^{187}Os/^{188}Os$ measurement from the N-TIMS data, assuming a IUPAC $^{188}Os/^{189}Os$ ratio (Meija *et al.* 2016b), is within the calculated uncertainty (2s) of the atom probe measurement results of HSE1 SYN1 and SYN2. However, the atom probe measurement results of $^{187}Os/^{189}Os$ from HSE2 is slightly lower than the N-TIMS ratio and sits outside the calculated uncertainty (2*s*) (see Table 4). Varying the width of the peak range, results in the same depleted ratio. HSE1 and HSE2 overlap each other within the calculated uncertainty (2*s*). There are three possibilities which could account for a low APM $^{188}Os/^{189}Os$ ratio compared to N-TIMS: a systematic depletion in the APM data caused by the peak deconvolution of ^{187}Re-^{187}Os, contamination of the N-TIMS sample post extraction from the resin block prior to N-TIMS analysis, or an inhomogeneous distribution of $^{187}Os/^{189}Os$ within the reference material.

The measurement results of the pure element samples show no bias between N-TIMS and APM for Re and Os, therefore the peak deconvolution should not have a significant effect. It is possible the diamond wire saw used to cut the alloy for N-TIMS analysis may have introduced contamination. However, due to the mass fraction of Os in the alloy, this contamination would have to be large, which makes such a scenario unlikely. The alloy itself

was produced synthetically by Schwander *et al.* (2015) through melting pure elements together in an electric arc furnace. The final product is poly-phase (Figure 1). It is possible that the other HSE metals may have contained impurities of Os with variable $^{187}Os/^{189}Os$ that were not homogenised during the formation and quenching of the alloy. As N-TIMS measures the bulk sample and APM only samples a very small region, it is possible that the N-TIMS results are an average $^{187}Os/^{189}Os$ for the sample while APM sampled a depleted phase in an isotopically inhomogeneous alloy. The final run products of Schwander *et al.* (2015) SYN1 and SYN2 were re-heated to > 1600 °C which may have homogenised any isotopic heterogeneity. SYN1 and SYN2 are within 1% of the N-TIMS measurement results and much closer than the HSE1 and HSE2 (Table 4). This suggests the original alloy was isotopically heterogeneous and HSE2 sampled a low $^{187}Os/^{189}Os$ region relative to the bulk alloy as measured by N-TIMS. These all suggest that APM is reliably reproducing Re-Os isotopic fractions and can detect small volume isotopic heterogeneities within complex samples to within 1% (Table 4).

Re-Os isotope systematics and model ages

The samples analysed here are synthetic and therefore evaluation of their radiogenic 'ages' contain no real information. However, it is important to demonstrate that these results can be used to determine ages of similar geological samples and propagate associated uncertainties. Radiogenic isotopic systems exhibit per cent-level variations, which are discernible using our current data reduction methodology. Traditional Re-Os geochronology uses ^{188}Os to normalise the radiogenic nuclides. However, due to the potential overlap with Mo^+ ions, ^{189}Os was used in this study. ^{189}Os was used as it does not have an overlap with Mo^+ and it is also an odd-numbered isotope. Thus, all isotopes used to extract isotopic ratios for Re-Os

geochronology (^{185}Re, ^{187}Re, ^{187}Os and ^{189}Os) are of this nature. The reference materials used are of terrestrial origin and are either pure Os or synthetic samples. We can therefore calculate a Re depletion age for these samples based on the ^{187}Os/^{189}Os ratio of the sample and chondritic fractions from Lodders (2003) (Equation (6) adapted from Shirey and Walker (1998)).

$$T_{RD} = \frac{1}{\lambda} ln \left(\left(\frac{\left[\frac{^{187}Os}{^{189}Os}_{chondrite} - \frac{^{187}Os}{^{189}Os}_{sample} \right]}{\frac{^{187}Re}{^{189}Os}_{chondrite}} \right) + 1 \right) \quad (6)$$

HSE1 and HSE2 have Re depletion ages of 3.6 ± 0.9 Ga and 4.2 ± 0.7 Ga, respectively; while SYN1 and SYN2 have Re depletion ages of 3.2 ± 2.9 Ga and 2.6 ± 1.2 Ga, respectively. The Re depletion age for the HSE-alloy measured by N-TIMS is 2.7 ± 0.06 Ga (Figure 16). Os1 has a supra chondritic ^{187}Os/^{189}Os ratio. A Re depletion age therefore, cannot be calculated as Os1 evolved with elevated Re/Os prior to refinement into the pure alloy and its initial Re/Os ratio is not known.

These results indicate that APM can reproduce Os isotope ratios that are within 1% of the N-TIMS measurements and can therefore be utilised in Re-Os geochronology.

Recommended data reduction sequence for isotopic analysis using APM

Through evaluation of the above standards we have demonstrated that the isotopic fractions of elements in APM datasets can be affected by a number of variables. We have evaluated several of these and corrected for them to reliably reproduce isotopic fractions of Os and Re for several standard materials. Based on the findings of this study, the following is proposed as a general best practice for the reduction of isotopic data for Re and Os from APM:

1. Use the constant width method for ranging isotopic peaks.
2. Where possible, analyse simple materials to observe how they behave in the APM – usual charge states and complex ions.
3. Assess the degree of hydride production and correct if necessary.
4. Choose the isotope with the lowest fraction and element in the system and use odd numbered isotopes where possible to correct isobaric interferences. For Re-Os isobaric interferences:
    a. Correct for W
    b. Then correct for Pt using ^{195}Pt
    c. Then correct for Re using ^{185}Re and $^{187}Re/^{185}Re$.
    d. Calculate final $^{187}Os/^{189}Os$.
5. Evaluate the possibility of hidden overlaps in the spectrum.
6. Corroborate results on suitable standard materials with techniques such as N-TIMS.

The methods employed here produce isotopic fractions for Re and Os isotopes which are within 1% of the expected IUPAC fractions, and in many cases are lower.

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Figure captions

Figure 1. Backscattered electron (BSE) images of the reference samples (A) Pure Os wafer. (B) Zoom in of APT lift out site (blue box) (C) Pure Re wire. (D) Zoom in APM lift out site of Re wire (blue box). The variable contrast in the BSE image is due to different orientations of crystals in the alloy. (E) Multi-HSE alloy from Schwander *et al.* (2015). (F) A Higher magnification image of the multi-HSE alloy. Here we observe that the alloy is quite heterogeneous with at least three distinct phases.

Figure 2. (A–C) In-beam secondary electron images of the final polished APM specimens from the Re wire (Re1 and Re2), and the Os wafer (Os1), respectively. The red boxes indicate the regions sampled by APM. (D–E) Atom clouds of the APM data from specimens Re1 and Re2, respectively. The distribution of ^{185}Re is shown by the red spheres and ^{187}Re is shown by the green spheres. (F) Atom cloud of the APM data from specimen Os1. The distribution of ^{187}Os is shown by the red spheres and ^{189}Os is shown by the green spheres.

Figure 3. (A–B) In-beam secondary electron (SE) images of the final polished APM specimens from the multi-HSE alloy (HSE1 and HSE2) respectively. The red boxes indicate the regions sampled by APM. (C–D) Atom clouds of the APM data from specimens HSE1 and HSE2, respectively. Distributions of Os is shown by the red spheres and Re is shown by the blue spheres.

Figure 4. Images of APM samples SYN1 and SYN2. (A) BSE image of the multi-phase alloy derived from the run products of the experiments detailed in Schwander *et al.* (2015). The alloy is heterogeneous with Mo-rich and Pt-rich regions. The locations of APM samples SYN1 and SYN2 extracted from the Pt rich region are given by the red circles. (B) In-beam

SE image of the final polished APM specimen for SYN1 (C) In-beam SE image of the final polished APM specimen for SYN2. The Pt-weld was applied to the sample during sample preparation by a gas injection system to attach the specimen to the Si post.

Figure 5. A graph depicting the change in relative uncertainty s_A with increasing counts as defined by the power law in Equation (2) (orange). The effect of incorporating a background count of 100 into the uncertainty calculation (blue). An elevated uncertainty is calculated where total counts are less than an order of magnitude above background counts.

Figure 6. Graph depicting the variation in the calculated uncertainty (2*s*) in APM measurements of element X expressed in δ notation assuming equal fraction of the two isotopes ^{1}X and ^{2}X calculated using Equation (4). The orange shaded area of the plot represents the uncertainty in +ve δ and the blue shaded area represents the uncertainty in -ve δ.

Figure 7. Mass to charge state ratio (*m/z*) spectrum for Os1 in the 90–100 *u* range where Os^{2+} ions are present. These Os peaks are ranged using the full width method.

Figure 8. Mass to charge state ratio (*m/z*) spectrum for Os1 in the 90–100 *u* range where Os^{2+} ions are present. These Os peaks are ranged using the constant width method. Each peak range was set to 0.25 u. There is a slight peak at 95.5 *u* from a small mass fraction of Os-hydride polyatomic ions.

Figure 9. Mass to charge state ratio (*m/z*) spectrum for Re1 in the 90–100 *u* range where Re^{2+}ions are present. These Re^{2+} peaks are ranged using the constant width method. Each

peak range was set to 0.35 u. There are slight peaks at 83 and 84 *u* from a small mass fraction of Re-hydride polyatomic ions.

Figure 10. Graph depicting the relative fraction of the stable Os isotopes compared to IUPAC values from Meija *et al.* (2016b). The constant width method produces fractions marginally closer to the true isotopic values than the full width method.

Figure 11. The $^{187}Re/^{185}Re$ of Re1–2 relative to the total counts for Re^{2+} and Re^{3+} ions. There is no isotopic fractionation of isotopes between charge states, and both samples produce the expected IUPAC isotopic ratios consistent with N-TIMS measurements (shaded grey region).

Figure 12. Mass to charge state ratio (*m/z*) spectrum for HSE 1 in the 90–100 *u* range where Re^{2+}, Os^{2+}, Ir^{2+}, Pt^{2+} and W^{2+} ions are present. The table above reveals the complexity of a spectrum containing multiple elements that results in isobaric interferences.

Figure 13. Isotopic fractions of Os^{2+} from HSE1 relative to IUPAC isotopic fractions (Meija *et al.* 2016b) using different isobaric interference correction methods shown to 95% confidence. Deconvolutions using $^{189}Os^{2+}$, with and without a Pt^{2+} correction are shown in black and purple, respectively. $^{184}Os^{2+}$ and $^{186}Os^{2+}$ fractions calculated by assuming IUPAC ^{182}W and ^{183}W are shown in red and blue, respectively. The graph on the left-hand side shows the large anomalies produced through the W^{2+} deconvolutions of the lighter Os^{2+} isotopes. The graph on the right-hand side is cropped to show detail in the heavier Os^{2+} isotopes as the ^{184}Os and ^{186}Os relative fractions from the W deconvolution were large.

Figure 14. Isotopic fractions of Os^{2+} from HSE1 relative to IUPAC (Meija *et al.* 2016b). The effect of using different isotopes of Os (^{188}Os (red), ^{189}Os (black), ^{190}Os (blue) and ^{192}Os (purple)) to deconvolve the isobaric interference by different isobaric interference correction methods is shown.

Figure 15. Os isotope relative fractions from HSE1-2 compared with IUPAC fractions (Meija *et al.* 2016b). This reveals consistent isotopic measurements within the uncertainty (2*s*) of the counting statistics between the two APM specimens, indicating that APM isotopic determinations are reproducible.

Figure 16. Os isotopic ratio vs. model age plot of APM measurements of HSE1-2 and SYN1-2 alongside N-TIMS measurement for this alloy showing Re depletion ages. HSE1-2 was slightly depleted in ^{187}Os/^{189}Os relative to the N-TIMS measurement while SYN1-2 was in agreement with N-TIMS within the analytical uncertainty.

Table 1.

Operating conditions of the Geoscience Atom Probe at Curtin University for reference materials Os1, Re1, Re2, HSE1, HSE2, SYN1 and SYN2

Specimen	Hits	*T* (K)	Laser E (pJ)	Pulse frequency (kHz)	DR%
Os1	5294379	70	200	250	0.5
Re1	2710619	70	150	200	0.5
Re2	2756837	70	100	200	0.5
HSE1	18272218	60	100	200	0.5
HSE2	38250642	60	100	200	0.5
SYN1	1167754	60	40	200	0.5
SYN2	15000601	60	50	200	0.5

Hits relate to the number of ion detections during the analyses.

T relates to the temperature the specimen was held at in K.

Laser E is the energy of the pulsing laser in pJ.

Pulse frequency is the number of laser pulses per minute given in kHz.

DR% is the detection rate of laser pulses that result in the field emission of an ion leading to a detection event as a percentage.

Table 2.

Bulk chemistry of Re1 and Re2, Os1, HSE1, HSE2, SYN1 and SYN2 determined by evaluation of the APM *m/z* spectrum measurement results in atoms/100 atoms (at.%)

Specimen	Element													
	Re	Os	W	Ir	Mo	Ru	Pt	Rh	Ni	Co	Fe	Cr	Al	Si
Os1		99.9									0.1			
Re1	100.0													
Re2	100.0													
HSE1	3.0	9.7	7.6	8.2	28.9	23.9	2.2	0.0	2.7	0.0	13.6	0.0	0.0	0.0
HSE2	2.9	9.6	7.6	8.2	29.0	23.9	2.2	0.0	2.8	0.0	13.8	0.0	0.0	0.0
SYN1	1.2	10.6	0.7	2.9	5.4	26.3	0.02	0.0	0.0	0.0	1.3	0.1	5.4	45.9
SYN2	0.2	3.3	0.3	5.7	3.7	11.8	0.4	0.0	3.9	0.0	19.8	0.0	2.8	46.2

Associated 2*s* uncertainties were < 0.1% for all element measurement results.

Table 3.

N-TIMS measurement results for the pure Os (Os Metal) and multi-HSE alloy (HSE)

Sample ID	**$^{186}Os/^{188}Os$ ***	**± *s***	**$^{187}Os/^{188}Os$ ***	**± SE**	**± *s***	**$^{189}Os/^{188}Os$ ***	**± *s***	**$^{190}Os/^{188}Os$ ***	**± *s***	**$^{192}Os/^{188}Os$ ***	**± *s***
Os Metal	0.119823	0.000064	0.141774	0.000003	0.000058	1.21962	0.00009	1.98649	0.00009	3.09598	0.00033
Os Metal bis	0.119946	0.000072	0.141787	0.000008	0.000078	1.21978	0.00010	1.98646	0.00012	3.08797	0.00025
Average			**0.14178**		**0.00007**						
s			**0.00001**								
2*s*			**0.00002**								
HSE	0.11991	0.00009	0.10708	0.000021	0.00006	1.21935	0.00019	1.9865	0.0002	3.0880	0.0006
HSE bis	0.11982	0.00008	0.10701	0.000013	0.00004	1.21939	0.00008	1.9864	0.0001	3.0860	0.0003
Average			**0.10704**		**0.00005**						
s			**0.00005**								
2*s*			**0.00010**								

* Os isotope ratios are not oxygen corrected, and *s* is the standard deviation and SE refers to the standard error of the mean.

Table 4.

Re and Os isotope ratios for all samples analysed by APM using the data reduction methods established above ± 2*s*. N-TIMS measurement results of these specimens are also shown

APM sample	$^{187}Os/^{189}Os$	$^{187}Re/^{185}Re$
Re1	-	1.665 ± 0.006
Re2	-	1.672 ± 0.007
N-TIMS Re	-	1.674 ± 0.001
Os1	0.116 ± 0.003	-
N-TIMS Os	0.1162 ± 0.0002	-
HSE1	0.083 ± 0.005	-
HSE2	0.079 ± 0.004	-
SYN1	0.085 ± 0.0151	-
SYN2	0.088 ± 0.0062	-
N-TIMS HSE	0.0878 ± 0.0003	-